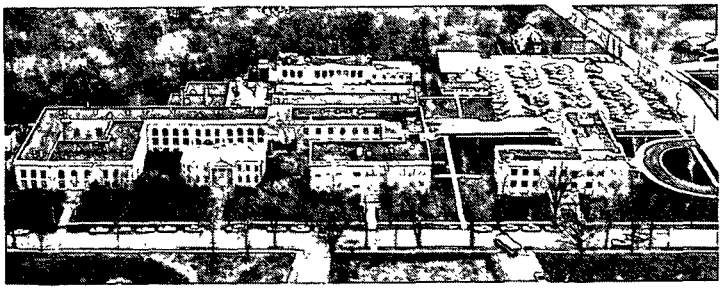

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 265

KRAFT WHITE LIQUOR COMPOSITION AND LONG TERM CORROSION BEHAVIOR

DAVID C. CROWE AND RONALD A. YESKE

NOVEMBER, 1987

Kraft White Liquor Composition and Long Term Corrosion Behavior

David C. Crowe and Ronald A. Yeske

This manuscript is based on results of IPC research and will be presented at the Corrosion/88 Conference sponsored by the National Association of Corrosion Engineers, and published in Materials Performance

KRAFT WHITE LIQUOR COMPOSITION AND LONG TERM CORROSION BEHAVIOR

David C. Crowe and Ronald A. Yeske
The Institute of Paper Chemistry
P.O. Box 1039
Appleton, Wisconsin 54912

ABSTRACT

The polarization behavior, long term weight loss and behavior of the corrosion potential of carbon steel in simulated kraft white liquor were investigated. Conditions relevant to white liquor storage and handling included NaOH + Na_2S solutions at 90 C with additions of $Na_2S_2O_3$, S and Na_2SO_3 individually and in combinations. Additions of S to form polysulfide produced high initial corrosion rates but eventually assisted passivation. Thiosulfate increased corrosion rates and impaired passivation. Sulfite slowed the rate of passivation. In liquors containing thiosulfate and sulfur, corrosion rates were lower than if either species was present individually. Combinations of thiosulfate and sulfite produced corrosion behavior most like that in actual mill liquor.

INTRODUCTION

Corrosion causes considerable damage to steel equipment used in kraft white liquor processing in pulp mills and so has been the subject of many previous studies. These have shown that increasing concentrations of NaOH and Na_2S, the principal components of white liquor, cause higher corrosion rates[1-3]. Mueller[4,5] utilized anodic polarization curves to study the active-passive nature of steel in white liquor. The polarization behavior of carbon steel in NaOH + Na_2S solutions was studied also by Tromans[6] in an effort to better understand the mechanisms of corrosion. Passivation was found to be inhibited by the incorporation of the sulfide ion into the passivating Fe_3O_4 film. This effort was extended to higher temperatures by Crowe and Tromans[7]. The active-passive current peak was associated with the formation of a soluble iron sulfide species. Full passivation required the formation of an Fe_2O_3 film.

Corrosion tests were performed in 180 mL fluorinated ethylene propylene (FEP) jars with screw-top lids. Each vessel contained four 1018 carbon steel test electrodes, each with a surface area of 9 cm^2. The electrode holders were constructed of polytetrafluoroethylene (PTFE) and the electrodes were isolated from the holder by ethylene propylene gaskets. The composition of the steel was 0.16 wt.% C, 0.68% Mn, 0.06% Si, 0.008% P, 0.024% S and the balance iron. The electrodes were polished to 120 grit prior to the test. Each cell also contained a silver-silver sulfide reference electrode (SSSE)[16]. Potentials measured versus the SSSE may be converted to the standard hydrogen scale (SHE) via the empirical equation:

$$V(SHE) = V(SSSE) - 0.7125 - 0.039 \log([Na_2S]/858)$$

where $[Na_2S]$ is the concentration of Na_2S in g/L.

Electrode potential was measured daily versus the reference SSSE. Test solutions were changed under nitrogen each week for solutions containing polysulfide and at 2-week intervals for other solutions. One of the electrodes was removed every 2 weeks, cleaned, and weighed to determine the corrosion rate by weight loss. Polarization curves were scanned at 1 mV/s using a Princeton Applied Research model 350 corrosion measurement system.

Regression equations were calculated for corrosion rates, but correlation coefficients, R^2, were low due to scatter in measured values and nonlinearity of corrosion rate with concentration of corrosive species (especially polysulfide and sulfite). Due to the poor correlation, the regression equations have not been reported here.

RESULTS AND DISCUSSION

NaOH + Na_2S Solutions

The anodic polarization behavior for steel in liquor containing 100 g/L NaOH + 30 g/L Na_2S is illustrated in Figure 1 as a representative example. The features of the polarization curve have been interpreted in previous work[7]. Three major anodic current peaks were observed. One, at -150 mV(SSSE), corresponds to thermodynamic potentials for Fe_3O_4 and $Fe(OH)_3^-$ formation. The magnitude of this peak was approximately constant through the range of solution compositions tested. The peak located between -60 and 0 mV(SSSE) was the largest, increasing in size and potential as Na_2S concentration increased. It is consistent with formation of FeS_2 from FeS and HS^-. The third current peak, at 30-60 mV(SSSE), is consistent with formation of Fe_2O_3 or FeOOH and remained the same size throughout the range of test solutions.

The results of weight loss tests in NaOH + Na_2S solutions are summarized in Figure 2. Corrosion rates ranged from 0 to 5 mpy in these binary liquors, compared with rates of 20 to 50 mpy typically measured in mills[17]. Slightly higher corrosion rates were observed in the first two weeks as the electrode potential moved from the active to passive region.

Plots of corrosion potential versus time showed that as the concentrations of Na_2S and NaOH increased the electrodes passivated more slowly or not at all, apparently because of increased dissolution and interference with passive film formation. However, the rate of dissolution remained relatively low in spite of a failure to passivate.

These results formed the basis for the study of liquor additions.

Thiosulfate Additions

In solutions containing thiosulfate, the polarization curves exhibited anodic current peaks at -150, -50, 75 and 165 mV(SSSE). The peak at 165 mV(SSSE) could not be related to a specific anodic reaction due to the large number of reactions possible near this potential; the other peaks have been identified for binary NaOH/Na_2S liquors. In general, thiosulfate additions increased the size of all the peaks, indicating that it increased rates of anodic reaction. As thiosulfate concentrations increased, the corrosion potential increased from -240 to -140 mV(SSSE), placing the corrosion potential in the active/passive range and closer to the redox potential for thiosulfate and bisulfide[16,18]. By increasing the potential into the active/passive range, the thiosulfate can cause increased dissolution.

Selected weight loss test results are illustrated in Figures 3 and 4. Figure 3 illustrates the dramatic increases in corrosion rates with thiosulfate additions, particularly in solutions with high sulfide concentrations. This result confirms the observation[19] that liquors are more corrosive when high concentrations of Na_2S and NaOH are present in mill liquor. Corrosion rates also increased with increasing NaOH concentration. Corrosion rates remained constant with exposure time as shown in Figure 4, i.e., the electrodes did not passivate during the period. At lower sulfide concentration, corrosion rates decreased slowly with exposure time because the electrodes passivated quickly, that is, there was a burst of active corrosion at the start of the test followed by a long period of passive behavior.

Potential monitoring revealed that the corrosion potential was in the active/passive region throughout most of the tests, resulting in high corrosion rates throughout the exposure. An example of this behavior is illustrated in Figure 5, which shows passivation [potential above 0 mV(SSSE)] occurring only at the lowest thiosulfate concentration (2.5 g/L) after 4 weeks. Shifts in potential, seen after 300 h intervals in Figure 5, were coincident with exchange of test solution. Passivation after long periods was observed occasionally for liquors with $Na_2S_2O_3$ concentration above 5 g/L.

According to early work[8], thiosulfate should increase corrosion rates by generating low concentrations of polysulfide. If this were true, then very high concentrations of thiosulfate would generate more polysulfide and passivation should occur after a short period of exposure (as described below). This was not observed. Thiosulfate does not appear to increase corrosion via polysulfide generation. Instead, it increases corrosion principally by holding the potential in the active-passive range where dissolution rates are high and also by increasing the size of peaks.

The results obtained here indicate that the corrosion rate will be high where thiosulfate is formed by oxidation of sulfide, for example at the liquid/vapor line in pipes and tanks. The thiosulfate must be less that 5 g/L in order for the steel to passivate during a long-term exposure. Mill studies suggest a value less than 4 g/L would be desirable.

Sulfur (Polysulfide) Additions

Addition of sulfur to form polysulfide obscured the features of the polarization curve, Figure 6. The anodic peaks at approximately -150, -40 and 70 mV(SSSE) have been identified above. In general, the peaks were smaller, meaning a decrease in critical current for passivation. This decreased current has been attributed to the reduction of polysulfide[12].

Polysulfide had a strong influence on corrosion potential as previously

observed[12,20]. Corrosion potentials measured prior to the polarization tests were clustered at -250, -100, 60 and 130 mV(SSSE). These appear to coincide with various electrochemical reduction reactions at these potentials, shown schematically in Figure 6. The corrosion potentials at -250 mV(SSSE) were close to the calculated potential for hydrogen evolution at -284 mV(SSSE) [or -929 mV(SHE)] for a solution at this pH and temperature. This is good agreement considering that the hydrogen activity is unknown and liquid junction potentials have been ignored. The corrosion potential at -100 mV(SSSE) is in the same range as the potential for reduction of thiosulfate via

$$S_2O_3^{2-} + 8H^+ + 8e^- = 2HS^- + 3H_2O$$

The calculated potential for this reaction is -50 mV(SSSE) [or -695 mV(SHE)] at 90 C in 100 g/L NaOH + 30 g/L Na_2S with 0.1 g/L $Na_2S_2O_3$, a reasonable level of impurity for sulfide solutions. The corrosion potentials at 60 and 130 mV(SSSE) may correspond to polysulfide equilibria. For example, the peak at 60 mV(SSSE) is close to the calculated thermodynamic potential for

$$S_3^{2-} + 3H^+ + 4e^- = 3HS^-$$

which is 63 mV(SSSE) [or -582 mV(SHE)] in 100 g/L NaOH + 30 g/L Na_2S + 1 g/L S at 90 C.

Average Tafel slopes from polarization curves for steel were calculated to be B_a = 64 mV and B_c = 128 mV. The value of 64 mV indicated that the rate determining step for oxidation involves the passage of a doubly charged species for oxidation of steel or sulfides[18].

Some weight loss results are illustrated in Figure 7, showing the effects of both Na_2S and S concentration. Corrosion rates in the two-week exposures were highest when sulfur (polysulfide) additions were in the range 0.5-2 g/L, but these high rates declined as the test proceeded and the electrodes passivated. The effect of polysulfide concentration was more pronounced in solutions with higher sulfide and hydroxide concentrations with higher active-passive dissolution currents. Measured corrosion rates were lower after 8 weeks as illustrated in Figure 8 due to the large part of the exposure time spent in the passive region. If the potential was in the range -200 to -150 mV(SSSE), corrosion rates were high. In solutions containing 5-10 g/L S, passivation was almost immediate.

Polysulfides stimulate passivation because of their oxidizing nature. In solutions with increased HS^- and OH^-, more polysulfide was required to cause passivation. For example, in 60 g/L NaOH + 10 g/L Na_2S, 1 g/L S was sufficient but in 120 g/L NaOH + 10 g/L Na_2S, 5 g/L S was required. In solutions with higher HS^-, it took much longer for passivation to occur, probably due to the greater current that had to be passed to move through the larger anodic current peaks. Apparently, sufficient current to maintain the passive film can be supplied by reduction of polysulfide. During the exposure, polysulfide would be reduced and steel oxidized to cause the corrosion potential to increase. At some concentrations, polysulfide increases the corrosion rate by placing the potential in the active/passive region.

In batch cooks, the transient high corrosion rate experienced in solutions with low concentrations of polysulfide would be repeated each cycle, leading to high corrosion rates. This was observed by Ahlers[10]. In continuous processes this transient effect would not occur if polysulfide concentration is stable. In liquor with no polysulfide, fluctuations to low polysulfide concentrations (0.5-2 g/L) would lead to very high corrosion rates. On this basis, additions of emulsified sulfur would lead to high corrosion rates in white liquor and so should be avoided.

Sulfite Additions

The polarization curves revealed no change in behavior compared with sulfite free solutions except that corrosion potentials were slightly lower, so no curves have been reproduced here.

High corrosion rates were observed at 1-5 g/L Na_2SO_3 as illustrated in Figure 9. In the two week tests, sulfite had very little effect in solutions with less than 25 g/L Na_2S. Corrosion rates during 8-week exposures were higher than in the 2 week exposures. The highest corrosion rates were in 4-, 6-, and 8-week tests for solutions with less than 10 g/L Na_2SO_3. High rates resulted because the electrode moved from active to passive potential during the exposure, passing through the high current range. In general, sulfite slowed passivation and so played a more important role than has been thought previously.

Passivation was slow for solutions with more than 5 g/L Na_2SO_3 because the sulfite maintained the potential below the active-passive peak. Lower corrosion potentials were observed in solutions with sulfite, consistent with the low reversible potential for sulfite. The effect of slow passivation may be seen in Figure 10, where high corrosion rates were observed for 1-5 g/L Na_2SO_3 in 100 g/L NaOH + 40 g/L Na_2S only for the 8-week exposure. High rates accompanied passive film formation in the last 2 weeks. The potential moved upward by 125 mV during the last week. In 100 g/L NaOH + 10 g/L Na_2S + 1-2 g/L Na_2SO_3, passivation occurred after only 2-4 weeks, probably due to easier passivation at lower sulfide concentrations.

Roald[3,8] considered that the equilibrium between sulfite and thiosulfate via

$$S_2O_3^{2-} + HS^- = S_2^{2-} + SO_3^{2-} + H^+$$

influenced polysulfide concentration and thus corrosion rate. If sulfite scavenged polysulfide and increased thiosulfate, increased corrosion rate would be expected, but this was not observed. Sulfite had an effect of its own.

Sulfite increased corrosion rates by slowing passivation, resulting in a long-term effect. The effect is most significant with 1-5 g/L $Na_2S_2O_3$ in liquors containing more than 25 g/L Na_2S. Eventually passivation should occur. By slowing passivation, sulfite may increase the corrosive effect of oxidants such as polysulfide and thiosulfate.

The results of Kesler and Bakken[15] may be rationalized based on the present results. In their study, with less than 1 g/L Na_2SO_3, there would have been no influence on the corrosion potential; the electrodes probably passivated and experienced high corrosion rates during passive film formation. With more than 1 g/L Na_2SO_3, the corrosion potential was probably maintained in the active region so that low corrosion rates were experienced during their 48 h tests. If their tests had been longer, then higher corrosion rates would have been observed in solutions containing more than 1 g/L Na_2SO_3 as the electrodes started to move through the active-passive range.

Thiosulfate + Sulfur (Polysulfide) Additions

Additions of combinations of polysulfide and thiosulfate were examined to determine the possibility of a synergistic effect between these corrosive species. Both of them were found to be corrosive and it was thought that, because they are both oxidants, very high corrosion rates might be observed when both were present.

Polarization curves were similar to those illustrated in Figure 1. Current

peaks were not identified due to their large number, their irreproducibility and the shifting corrosion potential in these solutions. This type of behavior would be anticipated where the electrode surface is nonuniform or partially oxide covered, suggesting that reactions are not occurring uniformly over the electrode surface and that some areas may be partially passivated.

Corrosion rates were relatively high after a 2-week exposure in 120 g/L NaOH + 40 g/L Na_2S + 0-25 g/L $Na_2S_2O_3$ with 0.5-2 g/L sulfur (polysulfide) as shown in Figure 11. Wide variations in corrosion rates in this range of S concentration were observed. Higher corrosion rates were expected in the 1-2 g/L S range due to the effect of polysulfide, but the presence of thiosulfate did not increase these corrosion rates substantially. In 80 g/L NaOH + 20 g/L Na_2S base solution after 2 weeks exposure, the corrosion rate was low if thiosulfate exceeded 5 g/L and S exceeded 1 g/L as illustrated in Figure 12. This was surprising because either thiosulfate or polysulfide alone would have resulted in high corrosion rates. In more concentrated solutions with 120 g/L NaOH + 40 g/L Na_2S, corrosion rates were higher, especially for higher S concentration, Figure 11. After 8 weeks, the corrosion rate had decreased to low levels for solutions with polysulfide and thiosulfate, as seen in Figure 13. High corrosion rates were observed in solutions with no sulfur additions. If sulfur (polysulfide) was present, it cancelled the thiosulfate effect. In liquor with no thiosulfate, the highest corrosion rate was for 1 g/L S. When thiosulfate was present, no maximum at 1-2 g/L S was observed for the 8 week tests. These results demonstrated that when the thiosulfate and polysulfide are present together the corrosion rate is reduced. High corrosion rates resulted only if either thiosulfate or polysulfide were absent.

Potential monitoring showed that after a short period of exposure, corrosion potential moved up to the passive range. This occurred immediately with 5 g/L S but took about 6 days with 1-1.5 g/L S. The corrosion potential fluctuated most in solutions with 120 g/L NaOH, probably due to greater difficulty of passivation.

In general, corrosion rates were lower if the species were mixed than if either species was present alone. In long tests in weak liquor, thiosulfate additions often decreased corrosion rates. These results indicate that thiosulfate reduces corrosion rate in polysulfide solutions and polysulfide reduces corrosion rates in thiosulfate solutions. Apparently, the thiosulfate shifts the corrosion potential into the active/passive range. Normally, high corrosion rates would result, but reduction of polysulfide could shift the potential further upward, into the passive range. The polysulfide apparently speeded passivation so that high corrosion rates were not observed in the presence of thiosulfate. Maximum corrosion rates occurred at lower sulfur (polysulfide) concentrations when thiosulfate was present. At low polysulfide concentration, thiosulfate additions apparently boosted the corrosion potential sufficiently that passivation occurred quickly and corrosion rates were low.

Liquor with combinations of two additives displayed a more complex behavior than solutions with a single additive. The relative amounts of the two species influenced the corrosion rates and rates of passivation. Despite accelerating corrosion by themselves, combinations of thiosulfate and polysulfide did not cause high corrosion rates. Generally, in mills polysulfide concentration is low, so the thiosulfate would be observed to accelerate corrosion.

Thiosulfate + Sulfite Additions

In the liquors with thiosulfate additions alone, the corrosion potential tended to be in the active-passive region. Sulfite, on the other hand, kept the potential in the active region. These results suggested that a dynamic balance could exist

between these two species which would result in corrosion potential in the active-passive range, slow passivation and sustained high corrosion rates as a result. Thus, combinations of thiosulfate and sulfite were tested. A base liquor with 100 g/L NaOH + 40 g/L Na_2S was used.

Representative polarization curves are illustrated in Figure 14. The large number of current peaks and the variability in their heights was typical of behavior in these solutions at higher thiosulfate concentrations. This variability precluded identification of the peaks.

In weight loss tests, sulfite concentrations up to 5 g/L increased the corrosion rate but had less effect above 5 g/L as can be seen in Figure 15. Sulfite would have inhibited passivation, thereby maintaining the corrosion rate throughout the 8-week exposure. Based on Figure 16, sulfite appears to have decreased the effect of thiosulfate, perhaps by depressing the corrosion potential below the maximum of the active/passive peak. Normally, the redox potential for thiosulfate coincides with the active/passive peak maximum. Higher corrosion rates were observed as the thiosulfate concentration was increased (Figure 16), consistent with higher dissolution currents in the active/passive region with increasing thiosulfate and with control of potential at higher values. These values persisted throughout the test. Thus, sulfite may sustain the high corrosion rates due to the thiosulfate by slowing passivation.

Potential was monitored and found to be in the active region throughout the tests. Only the test with 25 g/L $Na_2S_2O_3$ + 2 g/L Na_2SO_3 passivated and then only after 7 weeks. This was different from the behavior when thiosulfate was present alone; in that case, passivation occurred after about 4 weeks. This indicated that sulfite played an important role in controlling the potential. Corrosion rates were in the range normally experienced in mills and behavior was complex like that observed in mill liquor, suggesting that thiosulfate and sulfite must be present to properly simulate a mill liquor. Sulfite, which is a minor constituent of mill liquor, may play a part in passivation processes.

CONCLUSIONS

1. Corrosion rates in NaOH + Na_2S solution were low but increased as NaOH and Na_2S concentration increased.

2. Thiosulfate increased corrosion rates significantly and controlled the potential in the active/passive region where dissolution was increased. The effect of thiosulfate may be minimized by preventing its formation via oxidation of reduced sulfur species. Levels should be maintained below 5 g/L to minimize its effect.

3. Low concentrations of polysulfides caused transient high corrosion rates but corrosion rates decreased in the long exposures. Passivation was immediate at higher polysulfide concentrations. Polysulfide may be formed by oxidation of liquor and due to its transient effect, it will be most troublesome where fluctuations in concentration occur often or the film is damaged due to high flow rate or mechanical abrasion. Additions of emulsified sulfur as a makeup chemical in the recausticizing area would be expected to result in high transient corrosion rates.

4. Sulfite increased corrosion rate especially at high sulfide concentration as passivation occurred. Higher corrosion rates are experienced as the electrode passes through the active/passive range. Sulfite generally slowed passivation.

5. Additions of combinations of thiosulfate and polysulfide led to lower corrosion rates than if either was present alone. They appeared to have a complementary effect in stimulating passivation.

6. Additions of combinations of thiosulfate and sulfite displayed the complexity of real mill liquor. The sulfite assisted in maintaining the corrosion potential in the active region. The corrosion rate was related to the thiosulfate concentration.

ACKNOWLEDGMENTS

The financial support provided by the members of The Institute of Paper Chemistry is gratefully acknowledged. This work would not have been possible without the diligent experimental efforts of Mike Heath and Jim Tierney.

REFERENCES

1. L. Ruus, L. Stockman, Svensk Papperstid. 56:857(1953).

2. L. Stockman, L. Ruus, Svensk Papperstid. 57:831(1954).

3. B. Roald, Norsk Skogind. 10:285-9(1956).

4. W. A. Mueller, Can. J. Tech. 34:162-81(1956).

5. W. A. Mueller, Tappi 40:129-40(1957).

6. D. Tromans, J. Electrochem. Soc. 127:1253-6(1980).

7. D. C. Crowe, D. Tromans, Paper 203, Corrosion 87, NACE, Houston (1987), accepted for publication in Corrosion.

8. B. Haegland, B. Roald, Norsk Skogind. 9:351-64(1955).

9. J. W. Hassler, Tappi 38:265-74(1955).

10. P. E. Ahlers, Pulp Paper Ind. Corr. Prob. 4:53-55(1983).

11. P. Landmark, B. Roald, Norsk Skogind. 15:342-7(1961).

12. D. A. Wensley, R. S. Charlton, Corrosion 36:385-8(1980).

13. W. A. Mueller, Pulp Paper Mag. Can. 74(4):69-76(1973).

14. L. Peterman, R. A. Yeske, Paper 201, Corrosion 87, NACE, Houston (1987).

15. R. B. Kesler, J. F. Bakken, Tappi 41:97-102(1958).

16. D. C. Crowe, D. Tromans, Pulp Paper Ind. Corr. Prob. 5:159(1986).

17. D. C. Crowe, R. A. Yeske, Matl. Perf. 25(6):18(1986).

18. D. C. Crowe, D. Tromans, to be published.

19. D. A. Wensley, Pulp Paper Ind. Corr. Prob. 5:15-22 (1987).

20. D. Singbeil, D. Tromans, Pulp Paper Ind. Corr. Prob. 3:40-46(1982).

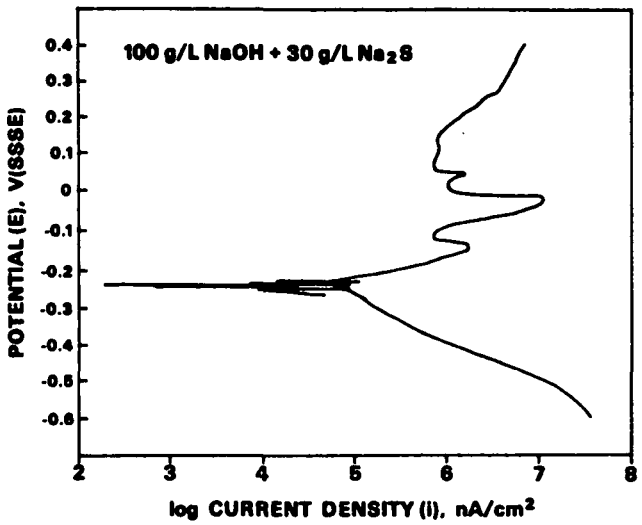

FIGURE 1 - Polarization behavior of carbon steel in NaOH + Na_2S solution.

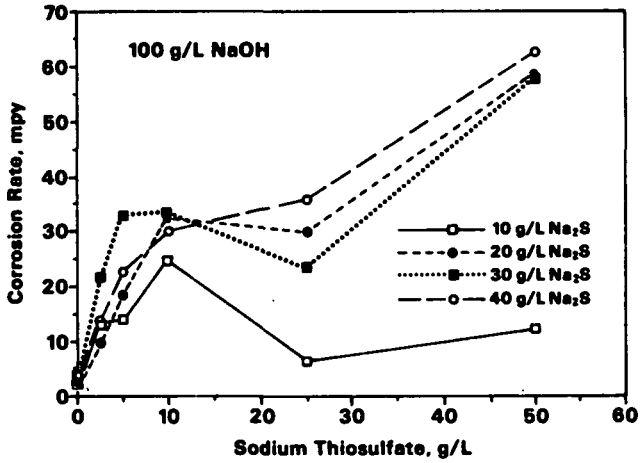

FIGURE 3 - Effect of variation of $Na_2S_2O_3$ and Na_2S concentration on corrosion rates after 2 weeks exposure.

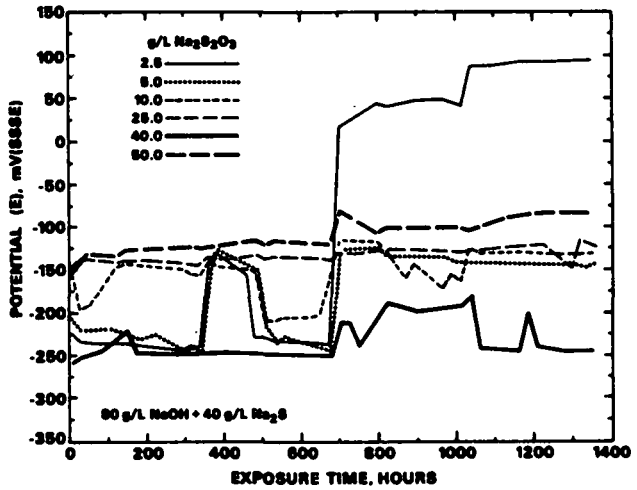

FIGURE 5 - Corrosion potential during exposure in 80 g/L NaOH + 40 g/L Na_2S with $Na_2S_2O_3$ additions.

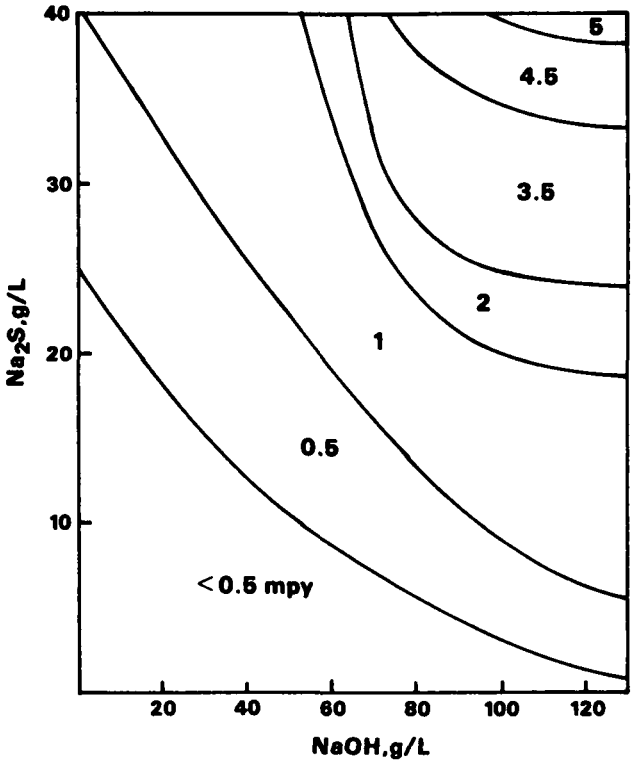

FIGURE 2 - Isocorrosion plot for NaOH + Na_2S solutions after 8 weeks exposure.

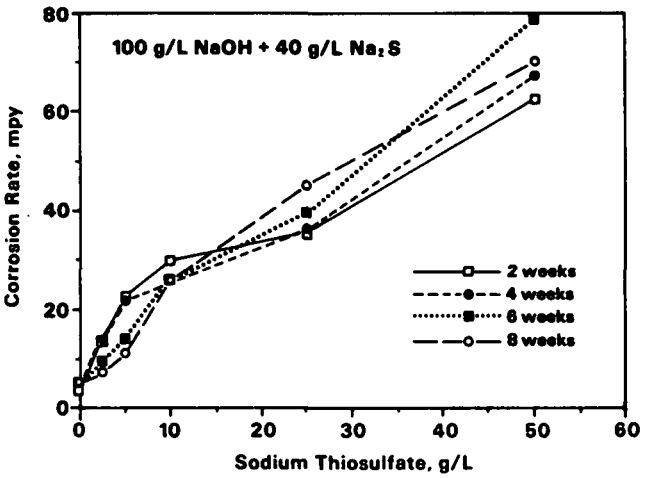

FIGURE 4 - Effect of variation in $Na_2S_2O_3$ concentration and exposure time on corrosion rates.

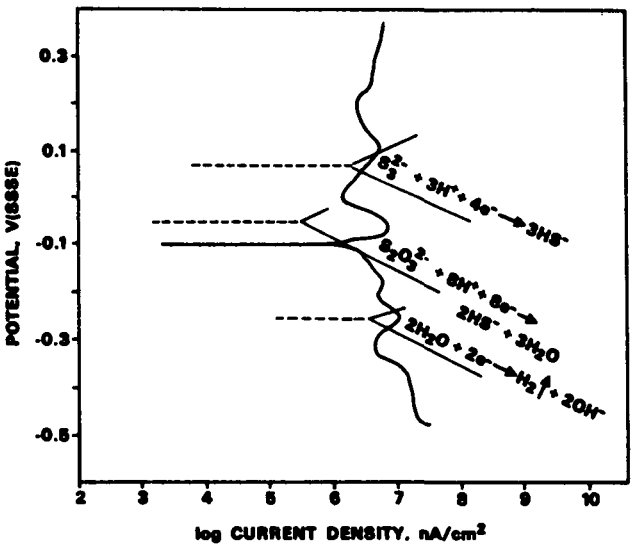

FIGURE 6 - Polarization curve in NaOH + Na_2S + S with schematic illustration of reactions which may determine the corrosion potential in polysulfide solutions.

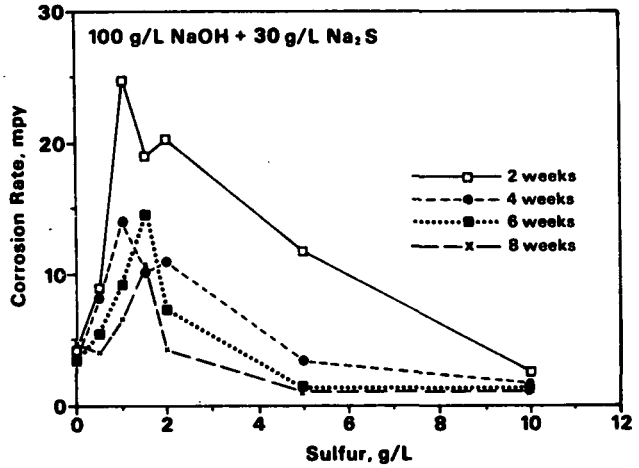

FIGURE 8 - The effect of sulfur (polysulfide) additions and exposure time illustrating the high corrosion rates experienced in solutions with 0.5-2 g/L S and how that effect is lesser in the longer term tests.

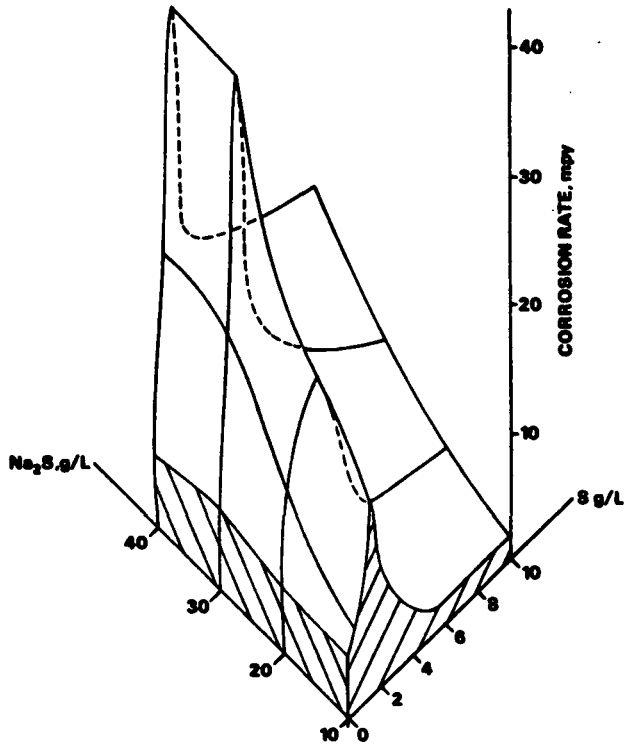

FIGURE 7 - Corrosion rates in 120 g/L NaOH solution with a range of Na_2S and S (polysulfide) concentrations after 2 weeks exposure.

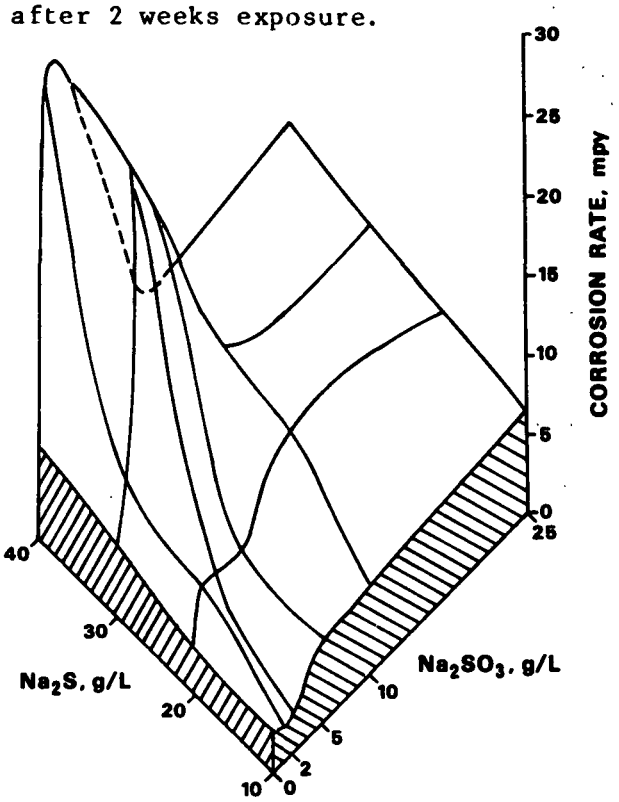

FIGURE 9 - Effect of sulfite additions and exposure time on corrosion rates in 100 g/L NaOH + 10-40 g/L Na_2S after 8 weeks exposure.

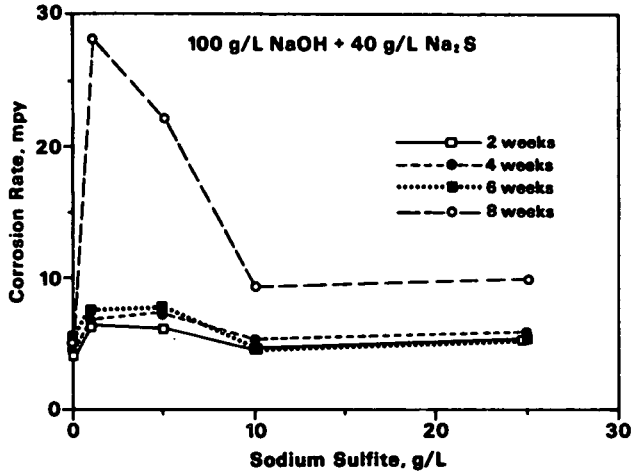

FIGURE 10 - Effect of sulfite additions and exposure time on corrosion rates. Highest corrosion rates were observed after 8 weeks as the electrode started to passivate.

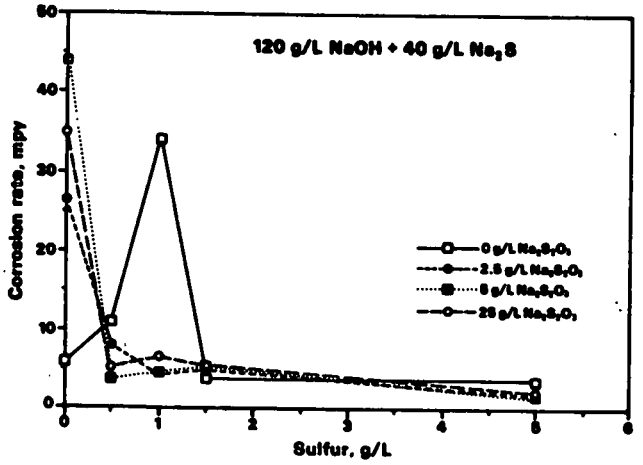

FIGURE 11 - Corrosion rate vs. S (polysulfide) and thiosulfate concentration in 120 g/L NaOH + 40 g/L Na_2S after 2 weeks exposure, showing the effect of polysulfide in these short-term tests.

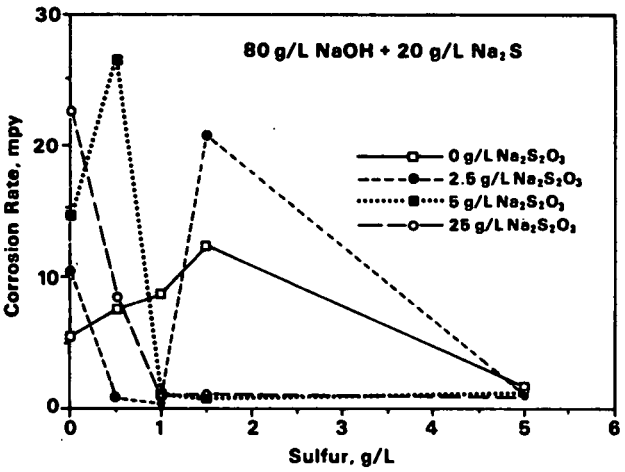

FIGURE 12 - Corrosion rate vs. S (polysulfide) and thiosulfate concentration in 80 g/L NaOH + 20 g/L Na_2S after 2 weeks exposure, showing the effect of polysulfide in these short-term tests.

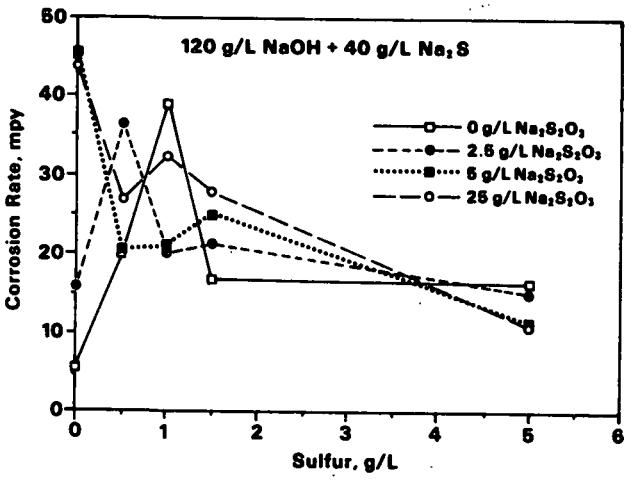

FIGURE 13 - The effect of S and thiosulfate concentration on corrosion rates in 120 g/L NaOH + 40 g/L Na_2S after 8 weeks exposure. The thiosulfate prevents the high corrosion rates at 0.5-2 g/L S.

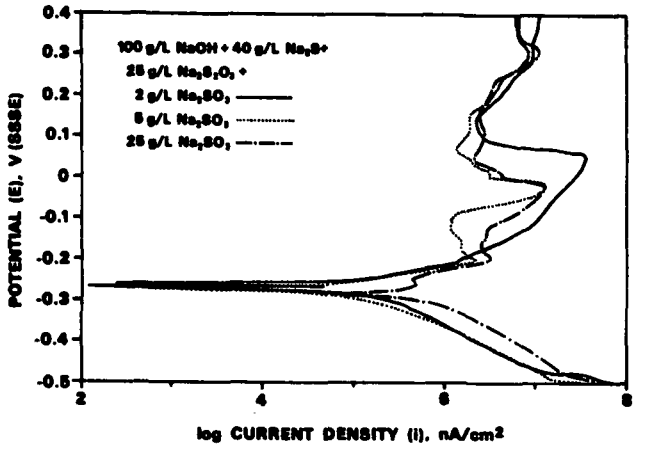

FIGURE 14 - In the solutions containing thiosulfate and sulfite, the polarization curves displayed more current peaks and more variability in the heights of peaks.

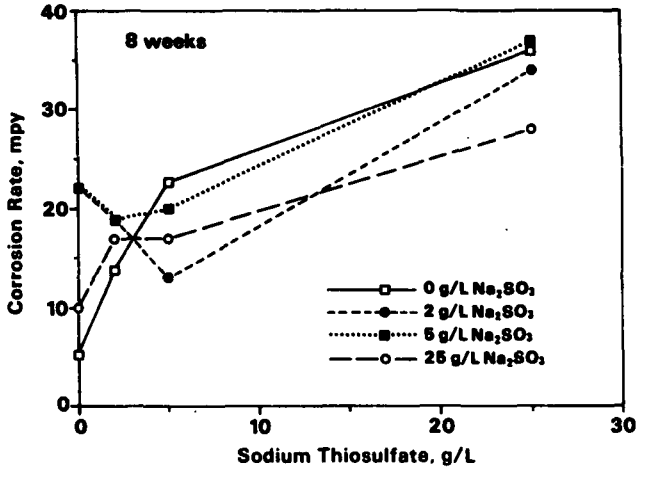

FIGURE 16 - Corrosion rates with additions of sulfite and thiosulfate after 8 weeks, illustrating the substantial effect of thiosulfate in these solutions (Base liquor: 100 g/L NaOH + 40 g/L Na_2S).

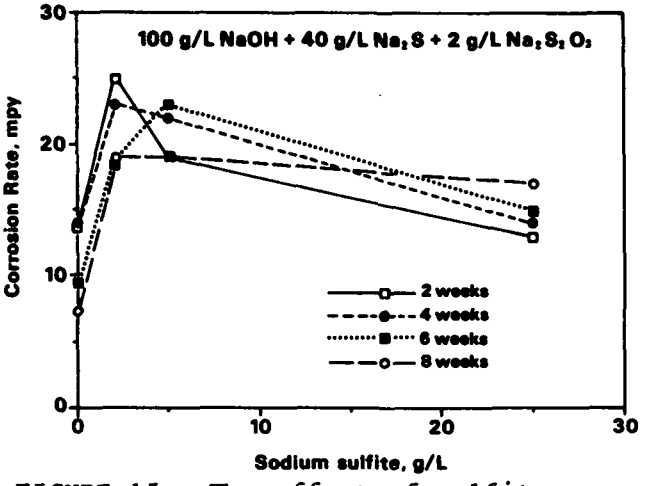

FIGURE 15 - The effect of sulfite concentration and exposure time on corrosion rates in 100 g/L NaOH + 40 g/L Na_2S + 2 g/L $Na_2S_2O_3$, illustrating the influence of sulfite concentration below 5 g/L and the lack of variation with exposure time.